THE UNIVERSITY OF PENNSYLVANIA

Some New Derivatives of Tungsten

THESIS

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Introduction.

As early as 1859 Blomstrand[1] reported a series of compounds of molybdenum derived from the dihalides $MoCl_2$ and $MoBr_2$. The dihalide was obtained by repeated volatilization of the trihalide in a current of carbon dioxide. The non-volatile product could be dissolved in alkalies and from this solution hydrates of the type $Mo_3Cl_4(OH)_2$ could be precipitated by weak acids. These compounds were yellow in color. They could be dissolved in strong acids, the nitric acid solutions showing no ionized halogen. The hydrochloric acid solution of the chloro-molybdenum hydroxide gave on crystallization $Mo_3Cl_6.6H_2O$ and on dilution a pale yellow insoluble compound $Mo_3Cl_6.3H_2O$. Mixed halogen derivatives such as $Mo_3Cl_4Br_2.6H_2O$ and $Mo_3Br_4Cl_2.6H_2O$ were also obtained. The chemistry and constitution of this class of compounds was further developed by Atterberg,[2] Liechti and Kempe,[3] Muthmann and Nagel,[4] Rosenheim and Kohn,[5] and Koppel.[6] Muthmann and Nagel determined the molecular weight of molybdenum dichloride dissolved in ethyl alcohol and found it to correspond to the triple formula Mo_3Cl_6. Rosenheim and Kohn prepared a compound, $Mo_3Cl_6.HCl.4H_2O$, by dissolving Mo_3Cl_6 in strong hydrochloric acid, evaporating on a water-bath and allowing the solution to crystallize. The compound consisted of glistening yellow needles, soluble in hydrochloric acid but hydrolized by pure water. Only three-sevenths of the chlorine in the compound was ionized.

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[1] Jour. prakt. Chem., **77** (1859), 88.
[2] Jahresbericht, **1872**, 260.
[3] Ann., **169** (1873), 354.
[4] Ber., **31** (1898), 2009.
[5] Z. anorg. Chem., **66** (1910), 1.
[6] Ibid., **77** (1912), 289.

In 1909 Chapin[1] published a paper on the Halide Bases of Tantalum. He prepared these compounds by a method previously used by Chabrié[2] for obtaining what he called the dichloride of tantalum. It consisted in heating the pentachloride with three per cent sodium amalgam in a hard glass tube sealed at one end and evacuated by means of a suction pump. Chapin used the pentabromide of tantalum. The reaction mass, taken up with water and hydrobromic acid and evaporated, furnished a crystalline body, $Ta_6Br_{14}.7H_2O$, dissolving in water to a dark emerald-green solution. Chapin further showed that only one-seventh of the bromine in this compound was ionized, indicating the formula $(Ta_6Br_{12})Br_2.7H_2O$. As further evidence of this formula he prepared a number of other derivatives of the radical Ta_6Br_{12}, *e.g.*, $(Ta_6Br_{12})Cl_2.7H_2O$, $Ta_6Br_{12}(OH)_2.10H_2O$ and others. He determined the molecular weight of the parent bromide in propyl alcohol and found it to correspond to the complex formula given.

In 1913 Harned[3] reported a similar series of compounds of columbium, obtained from the pentachloride by the Chabrié method. He obtained a crystalline body, $(Cb_6Cl_{12})Cl_2.7H_2O$, soluble in water to an olive-green solution, a crystalline hydroxide, $Cb_6Cl_{12}(OH)_2.8H_2O$, and others. Both the columbium and tantalum compounds were characterized by their remarkable tinctorial power, a milligram being sufficient to color one hundred cubic centimeters of water an intense green.

Harned also obtained a brown compound, insoluble in water, the analysis of which corresponded to the formula $Cb_6Cl_{14}.9H_2O$. This was prepared by the addition of concentrated hydrochloric acid to the alkaline solution of the green compound $(Cb_6Cl_{12})Cl_2.7H_2O$. The brown compound on boiling with water slowly reverted to the original

[1] J. Amer. Chem. Soc., **32** (1910), 323.
[2] Compt. rend., **144** (1907), 804.
[3] J. Amer. Chem. Soc., **35** (1913), 1078.

green. His experiments led him to the conclusion that there was a constitutional difference between the two.

In view of the existence of these compounds of molybdenum, tantalum and columbium, it would seem reasonable to expect that the closely related element, tungsten, would form some similar class of compounds. Roscoe[1] has reported the dichloride, dibromide and diiodide but a more thorough investigation of them has never been carried out. It was as an attempt to prepare compounds of tungsten similar to those of molybdenum, tantalum and columbium that the present work was undertaken.

Preliminary Work.

The preliminary work consisted of the following steps:

1. The preparation of pure tungsten trioxide from wolframite. The method of purification was that employed by Smith and Exner.[2]

2. The reduction of the trioxide to metallic tungsten by heating in pure hydrogen. The reduction was carried out in a quartz tube, heated to a little over 1000° in a gas-heated furnace constructed of asbestos. The metal obtained was of a pale gray color.

3. The conversion of the tungsten to hexachloride by heating in pure dry chlorine. The details of the process are fully described by Smith and Exner and need not be mentioned here. It was found, however, that, while a commercial tungsten could be converted to hexachloride at the rate of about twenty grams in two hours, the pure material obtained above was only very slowly attacked, seven hours being required to effect the chlorination of ten grams of metal. Since there was only a trace of oxychlorides formed in the reaction, it was thought that possibly their presence might exert a catalytic action on the chlorination. In an attempt to catalyze the reaction in

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[1] Ann., **162** (1872), 360.

[2] Chem. News, **90** (1904), 37.

another way, 0.1 gm. of precipitated platinum was sprinkled on the tungsten in the boat. On passing chlorine over the gently heated boat no difference in the speed of the reaction was at first noticed. After a few minutes a glow appeared to run through the mass and, from this point on, the reaction took place as fast as the chlorine could be passed in, the chlorine uniting with the metal with incandescence. By this means 20 gm. of tungsten could be converted to hexachloride in $1^1/_2$ to $1^3/_4$ hours. After the tungsten had been swept out, the platinum remained in the bottom of the boat as a brown powder. This was used in the chlorination of the next batch of tungsten and so on repeatedly. 300 gm. of pure tungsten hexachloride were so obtained.

Reduction of Tungsten Hexachloride by the Chabrié Reaction.

The method was essentially that outlined by Chabrié and by Chapin. The hexachloride was mixed in a mortar with a little less than the amount of powdered 3% sodium amalgam calculated to reduce it to the state of the dichloride. The mixture was quickly transferred to a Jena tube sealed at one end. The tube, after connecting with a suction pump and evacuating, was gently heated until the reaction had taken place and then heated strongly for about ten minutes. It was allowed to cool in the vacuum, and the contents extracted with hydrochloric acid. On filtering there was obtained a deep reddish brown filtrate and a gray precipitate. Attempts to crystallize the highly colored compound from this solution failed. The solution was very stable in the air and could be evaporated to dryness with only a trace of decomposition.

Before preparing any quantity of the brown solution the conditions of the reaction were investigated, varying the proportions of the reacting substances and the temperature and duration of heating. As a result the following details were adopted: 15 gm. of tungsten hexachloride were ground in a mortar and mixed carefully and quickly

with 105 gm. of sodium amalgam. The reaction between the two substances is a rather vigorous one and, unless precautions are taken to prevent it, is liable to take place in the mortar. In view of this, the mortar, as well as both of the reacting substances, were cooled in ice previous to the mixing. In addition to this, not more than ten seconds was allowed to elapse between the time when the amalgam was brought in contact with the hexachloride and the time when the mixture was in the Jena tube with the vacuum on. In spite of these precautions the reaction frequently took place during mixing. When the mixing and transfer to the tube had been successfully accomplished, the reaction was allowed to take place, and the tube then heated just to dull redness and allowed to cool immediately. The contents were extracted with hydrochloric acid (sp. gr. 1.08), and the solution filtered. The brown color so obtained was intense.

A portion of the brown solution was evaporated to dryness and the dry residue extracted with alcohol. A dark reddish brown solution was obtained from which nothing could be crystallized. An extraction with ether gave a yellow solution which on evaporation left a pale yellow amorphous substance. This, taken up with a drop of dilute hydrochloric acid and allowed to evaporate, showed under the microscope shining yellow needles. A somewhat larger portion of the dry residue, treated in a similar way, gave needles as much as a centimeter in length. Experiments with the original brown solution of the reduced mass led to the following method of isolation of the yellow needles: The brown solution was boiled down until considerable sodium chloride had separated out, when it was filtered hot and allowed to cool. There crystallized out a mixture of sodium chloride and the yellow needles. This was filtered off and washed with concentrated hydrochloric acid until the liquid came through almost colorless. The mixture was spread out on a watch glass and allowed to dry in the air. It was

then extracted for about ten minutes under a reflux condenser with ether containing about 5% of ethyl alcohol. The insoluble sodium chloride was filtered out and the ether distilled off from the filtrate, leaving a yellow amorphous mass. This was taken up with fairly strong hydrochloric acid and boiled, when everything dissolved. The clear yellow solution was evaporated to small bulk and allowed to cool, the yellow needles crystallizing out in large quantities. These were filtered off, washed with concentrated hydrochloric acid and dried in the air. From 150 gm. of tungsten hexachloride, 12 gm. of the yellow compound were obtained.

Properties of the Yellow Needles.

The compound was readily soluble in alcohol, acetone, glacial acetic acid and in ether containing alcohol, but almost insoluble in pure anhydrous ether. It was insoluble in benzene, carbon bisulphide, carbon tetrachloride and chloroform. It dissolved in water but the aqueous solution on standing hydrolyzed, precipitating out first a yellow and then a black compound. The crystals on long exposure to air or in a desiccator over sulphuric acid disintegrated, giving a lemon-yellow amorphous compound, insoluble in water. The same compound was produced on allowing the solution in dilute hydrochloric acid to stand or on diluting it with water. The resemblance of these two compounds to Rosenheim and Kohn's $Mo_3Cl_6.HCl.4H_2O$ and Blomstrand's $Mo_3Cl_6.3H_2O$ will be at once noticed.

Nitric acid on warming effected a complete decomposition of a solution of the yellow needles, a hydrated tungsten trioxide being precipitated out in a granular form. Potassium hydroxide added to an aqueous solution of the compound gave a clear yellow solution which darkened immediately to a deep brown. From this solution weak acids threw down a black gelatinous precipitate. The same compound was obtained by treating the aqueous

solution of the yellow needles with sodium carbonate. The brown alkaline solution on exposure to the air slowly faded in color to a deep yellow, which with weak acids threw down a yellow gelatinous precipitate.

Analysis of the Yellow Needles.

The determination of tungsten in the compound was obtained by a very simple and direct method. The compound was weighed out in a porcelain crucible, covered with concentrated nitric acid and digested for several hours on a water-bath. It was then evaporated to dryness, ignited and weighed as WO_3. Results 1 and 2 were obtained by this method. The analyses were run on different preparations of the compound, the results giving evidence both of the accuracy of the method of analysis and of the homogeneity of the product. The third determination was obtained by an altogether different method. The aqueous solution of the compound was treated with potassium hydroxide and the deep brown solution acidulated with acetic acid. The black precipitate was filtered off and ignited to trioxide.

No.	Wt. Sample.	WO_3 Found.	% W.
1.....	0.2223	0.1752	62.50
2.....	0.2271	0.1787	62.42
3.....	0.2009	0.1586	62.62
		Average =	62.51%

The determination of chlorine offered much greater difficulty. It would be fruitless to enumerate the methods attempted. Most of them were valueless for the reason that the silver chloride came down contaminated with tungsten. It might be mentioned here that the presence of as little as $^1/_2\%$ of tungsten in this precipitate completely alters its character, the silver chloride coming down granular rather than curdy. Of the methods attempted the following appeared to be the most satisfactory:

Method 1. The compound was dissolved in water, treated with ammonia and the solution oxidized with

ammonium persulphate. The excess ammonia was boiled off, the tungsten precipitated out as cadmium tungstate and the chlorine determined in the filtrate as silver chloride. Determination 1 was obtained by this method.

Method 2. The solution of the compound was treated with sodium carbonate and boiled. The black precipitate was filtered out and the silver chloride precipitated in the filtrate. The precipitate showed considerable contamination with tungsten and was dissolved in ammonia and reprecipitated. Determinations 2 and 3 were obtained in this way.

Method 3. The compound was dissolved in nitric acid (sp. gr. 1.1), and warmed for about two hours when the tungsten had completely separated as the hydrated trioxide. This was filtered off and the chlorine determined as silver chloride in the filtrate. The precipitate showed no contamination with tungsten. The results are determinations 4 and 5.

No.	Wt. Sample.	AgCl Found.	% Cl.
1.....	0.2039	0.2351	28.53
2.....	0.1999	0.2298	28.43
3.....	0.2014	0.2329	28.62
4.....	0.2022	0.2285	27.97
5.....	0.2015	0.2269	27.85
		Average =	28.28%

The water was determined by the method used by Chapin. The compound was mixed with dry lead oxide and heated in a boat in a current of pure dry air to about 300° for two hours. The water was collected in a weighed calcium chloride tube. The details of manipulation are those outlined by Chapin.

No.	Wt. Sample.	H_2O Found.	% H_2O.
1.....	0.2007	0.0203	10.11
2.....	0.2008	0.0206	10.26
		Mean =	10.18%

It should be noted here that the hydrogen of any hydrochloric acid in the molecule of the compound would appear

here as water along with the true water of the compound. The theoretical compositions calculated below are figured on this basis and will therefore add up to more than 100%.

Formula of the Yellow Compound.

It was expected that the composition of the compound would correspond to the formula $W_3Cl_6.HCl.4H_2O$ analogous to Rosenheim and Kohn's $Mo_3Cl_6.HCl.4H_2O$. It will be noticed on reference to the figures that the observed values do not agree with those calculated for this compound. They agree much better with the calculated percentages for a compound containing another half molecule of water, the doubled formula of which would be $W_6Cl_{12}.2HCl.9H_2O$. The calculated compositions follow:

Per cent.	Calculated for $W_3Cl_6.HCl.4H_2O$.	Calculated for $W_6Cl_{12}.2HCl.9H_2O$.	Observed.
W.....	63.20	62.55	62.51
Cl.....	28.46	28.16	28.28
H_2O.....	9.27	10.20	10.18

The doubled formula finds support in its analogy with the tantalum and columbium compounds. It finds a complete analogy in the columbium compound prepared by Harned and formulated by him, $Cb_6Cl_{14}.9H_2O$. His analysis, however, will be found to correspond just as closely to the composition $Cb_6Cl_{12}.2HCl.9H_2O$, his water determination lying just half way between the two formulas.

Attempt to Determine the Ionized Chlorine in the Yellow Compound.

Since the compounds of molybdenum, tantalum and columbium ionize only part of their chlorine in aqueous solution, it seemed reasonable to expect that the yellow tungsten compound would behave similarly. Accordingly an attempt was made to determine the amount of chlorine ionized. In view of the fact that the compound is hydrolyzed in pure water or in dilute acids other than hydrochloric, the problem presented considerable diffi-

culty. The first attempt was to dissolve the compound in potassium hydroxide solution and to add to the deep brown solution acetic acid, throwing out the black gelatinous precipitate. This was filtered off and the chlorine determined in the filtrate. The operation was conducted entirely in the cold. A similar treatment of the molybdenum compound precipitates a hydrated $Mo_3Cl_4(OH)_2$ leaving the ionized chlorine in the filtrate. The same behavior was expected here. The following result was obtained:

Wt. sample = 0.2009 AgCl found = 0.2291 % Cl = 28.21

The result corresponds to the total chlorine in the compound, indicating that a complete decomposition had taken place and that the black precipitate contained no chlorine.

A second attempt was based on the fact, previously mentioned, that the brown alkaline solution on standing fades to a brownish yellow, and that from this solution acetic acid precipitates a yellow compound. A sample of the yellow needles was dissolved in alkali and so treated, the chlorine being determined in the filtrate.

Wt. sample = 0.1017 AgCl found = 0.1182 % Cl = 28.76

The result again indicates a complete decomposition of the compound. It would seem probable that if compounds, in which only part of the chlorine is split off, are formed at all, they are extremely unstable.

Attempt to Determine the Molecular Weight of the Yellow Needles.

In order to provide further evidence in favor of the formula assigned to the yellow compound, a determination of the molecular weight was sought. An attempt was first made to arrive at this by the lowering of the freezing point of glacial acetic acid. It was found, however, that the water of crystallization of the compound interfered to such an extent that no result could be obtained

by this method. The rise of the boiling point of ethyl alcohol was next attempted. Here the hydrochloric acid in the molecule appeared to interfere, the boiling point falling on solution of the compound rather than rising. A further investigation along these lines was prevented by lack of material.

Other Related Compounds.

The lemon-yellow amorphous compound has been described. About a gram of this material was prepared from the yellow needles. The compound was soluble in boiling hydrochloric acid, reverting to the original yellow compound. It dissolved in alkalies to give the deep brown solution. Analysis gave the following results:

Wt. sample =	0.2003	WO_3 found =	0.1716	%W =	67.95
Wt. sample =	0.2074	AgCl found =	0.2325	%Cl =	27.73
	0.2007		0.2236		27.57
	0.1063		0.1169		27.20
Wt. sample =	0.2001	H_2O found =	0.0107	$\%H_2O$ =	5.35

The analysis fails to correspond to any reasonable formula and it is probable that the compound prepared was impure.

An investigation of the mother liquors from the crystallization of the yellow needles led to the isolation of another compound crystallizing in dark brown shining needles. This was prepared by slowly saturating the mother liquor with hydrochloric acid gas and letting it stand for several days. The sodium chloride thrown out contained, besides some yellow needles, a small quantity of the brown compound in crystals about 2 mm. long. The mixture was dried and the brown needles picked out. Only a few milligrams were obtained. The compound dissolved in water to a clear yellow solution, not decomposed by boiling nitric acid nor by potassium hydroxide. Sodium carbonate threw out a yellow granular precipitate. The tinctorial power of the compound was remarkable, one of the small crystals giving a decided color to 100 cc.

of water. This fact makes it rather probable that the compound is related to the tantalum and columbium compounds. No analysis was obtained owing to the small amount of substance at hand.

Investigation of the Alkaline Solution of the Yellow Needles.

It has been mentioned that the addition of alkali to an aqueous solution of the yellow needles produced three distinct solutions: first, a yellow solution which changed immediately to a deep brown which in turn changed slowly on exposure to the air to a less highly colored brownish yellow solution. It was undertaken here to determine the state of oxidation of the tungsten in these three. The deep brown solution was first investigated. To this end a sample of the yellow compound was dissolved in water and treated with a solution of potassium hydroxide. The solution was let stand for about thirty seconds when it had assumed the dark color. An excess of standard iodine was then added, the color fading to a pale yellow. After standing thirty minutes, the solution was made acid with acetic acid and the excess iodine titrated with thiosulphate. The result is No. 1 in the table. It shows that the tungsten is almost completely in the trivalent condition. The determination was repeated allowing the alkaline solution to stand ten minutes before the addition of the iodine. The result (2 in the table) shows that the tungsten has been completely oxidized to the trivalent state. Since, from the deep brown solution, weak acids throw out the black gelatinous precipitate which redissolves in alkali to give the original solution, the above results would show this black compound to be a hydrated W_2O_3, possibly $W(OH)_3$.

The same method was next applied to the brownish yellow solution obtained by letting the alkaline solution stand exposed to the air for twenty-four hours. The result (3 in the table) shows that the solution contains

quadrivalent tungsten and that the yellow hydrate obtained from it by the action of weak acids must be a hydrated WO_2.

The first yellow alkaline solution contains tungsten of undoubtedly the same state of oxidation as the yellow needles. The rapidity with which it oxidizes made it rather more difficult to investigate than the other two. To avoid this difficulty the iodine solution was added to the potassium hydroxide and the mixture then added to the water solution of the yellow compound. It was then let stand thirty minutes, made acid, and titrated as before. The result is No. 4. It indicates bivalent tungsten, which was of course to be expected.

No.	Wt. Sample.	I Absorbed.	Calc. for W″.	Calc. for W‴.	Calc. for W⁗.
1....	0.1007	0.138	0.174	0.131	..
2....	0.1008	0.131	0.174	0.131	..
3....	0.1016	0.089	..	0.132	0.088
4....	0.1009	0.167	0.174	0.131	..

Summary.

1. The action of chlorine on tungsten metal to form hexachloride is catalyzed to a remarkable degree by the presence of a small amount of platinum black.

2. Tungsten forms the compound $W_6Cl_{12}.2HCl.9H_2O$, resembling the molybdenum compound $Mo_3Cl_6.HCl.4H_2O$, prepared by Rosenheim and Kohn.

3. The alkaline solution of the above compound oxidizes readily and from the solution stable hydrates of trivalent and quadrivalent tungsten have been obtained.